QM/MM simulations of $Au_{25}(GSH)_{18}^-$ in aqueous environment

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The effects of aqueous solvent and biological ligands on the structural and electronic properties of thiolate-protected $Au_{25}(SR)_{18}^-$ clusters have been studied by performing quantum mechanics/molecular mechanics (QM/MM) simulations [1]. Analysis of bond distances and angles show that the solvated cluster experiences modest structural changes, which are reflected as flexibility of the Au core. The hydrophilic glutathione (GSH) ligands shield the metallic core effectively and distort its symmetry via sterical hindrance effects. We show that the previously reported agreement between the calculated HOMO−LUMO gap of the cluster and the optical measurement is due to cancellation of errors, where the typical underestimation of the theoretical band gap compensates the effect of the missing solvent. The use of a hybrid functional results in a HOMO−LUMO gap value of 1.5 eV for the solvated cluster with GSH ligands, in good agreement with optical measurements. Our results demonstrate that ligand/solvent effects should be considered for a proper comparison between theory and experiment [2]. Further simulations for ligand exchange reactions with a model peptide display selectivity effects with respect to the substituted GSH side group and the amino acid sequence (primary structure) of the protein terminal groups.

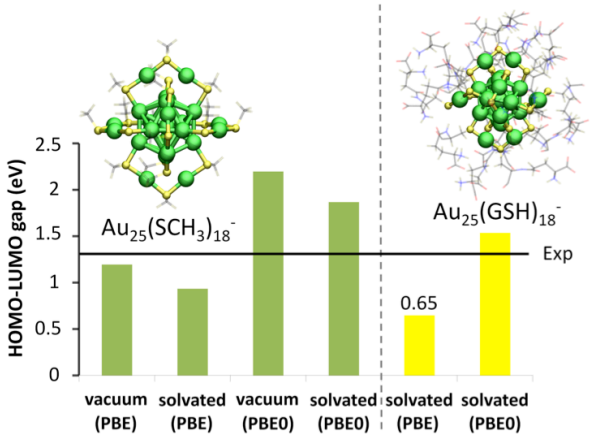

Figure 1: HOMO-LUMO gaps of $Au_{25}(SR)_{18}^-$ clusters in vacuum and solvated in water with PBE and PBE0 exchange-correlation functionals.

[1] A. Laio, J. VandeVondele, and U. Rothlisberger, *A Hamiltonian Electrostatic Coupling Scheme for Hybrid Car–Parrinello Molecular Dynamics Simulations*. J. Chem. Phys. **116**, 6941 (2002).

[2] V. Rojas-Cervellera, C. Rovira, and J. Akola, *How do Water Solvent and Glutathione Ligands Affect the Structure and Electronic Properties of $Au_{25}(SR)_{18}^-$?* J. Phys. Chem. Lett. **6**, 3859 (2015).